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The proposal described and requested funding for part of what is intended to become a larger system representing an optics-based research facility for ultrafast pulsed laser deposition and characterization of modulated films, coatings, and surface structures. An in-situ diagnostics approach is used as a process control, through real-time feedback, in manufacturing multilayer thin films and coatings. Experimental facilities employing optical techniques, in conjunction with other more conventional particle monitoring and control methods, provides new and advanced capability, as well as greater insight, into complex thin-film fabrication. Such insight has been, and continues to be, demanded by sophisticated industrial and government end users. The present program is aimed at establishing a multi-port pulsed laser vacuum deposition chamber with an in-situ multi-wavelength ellipsometer to be used as an optical diagnostic and feedback control device. This system will be attached to a versatile high average power ultrafast pulsed laser for the experimental development and fabrication of modulated thin-film materials and multilayers. It is intended to be a collaborative and interdisciplinary research facility set up at the Center for Ultrafast Optical Science at the University of Michigan.

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FINAL REPORT
AFOSR - DURIP '95
"Advanced Pulsed Laser Deposition System with *in-situ* Ellipsometric Diagnostics"
Award Reference Number
F49620-95-1-0474
Principal Investigator
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Abstract

The original proposal described and requested funding for part of what is intended to become a larger system representing an optics-based research facility for ultrafast pulsed laser deposition and characterization of modulated films, coatings, and surface structures. An in-situ diagnostics approach is used as a process control, through real-time feedback, in manufacturing multilayer thin films and coatings. Experimental facilities employing optical techniques, in conjunction with other more conventional particle monitoring and control methods, provides new and advanced capability, as well as greater insight, into complex thin-film fabrication. Such insight has been, and continues to be, demanded by sophisticated industrial and government end users. The present program is aimed at establishing a multi-port pulsed laser vacuum deposition chamber with an in-situ multi-wavelength ellipsometer to be used as an optical diagnostic and feedback control device. This system will be attached to a versatile high average power ultrafast pulsed laser for the experimental development and fabrication of modulated thin-film materials and multilayers. It is intended to be a collaborative and interdisciplinary research facility set up at the Center for Ultrafast Optical Science at the University of Michigan.

1.0 Introduction

This document is a final report for the project entitled "Advanced Pulsed Laser Deposition System with *in-situ* Ellipsometric Diagnostics" which was granted by the Air Force Office of Scientific Research (AFOSR). The project was sponsored under the 1995 Defense University Research Instrumentation Program (DURIP) with award reference number F49620-95-1-0474. A one year no cost extension was requested at the end of the 1996 fiscal year and granted by the AFOSR. A progress report was submitted in support of the equipment purchases that had been made up to the end of that first fiscal year. It was submitted in October of 1996 and is attached for reference as Appendix I.

1.1 Project Description

The proposal for this project requested funding for part of what was intended to become a larger thin film and multi-layer deposition system representing an optics-based research facility for ultrafast pulsed laser deposition and characterization of modulated films, coatings, and multi-layered structures. Motivation for the overall system was based on the fact that processing technology for deposition of advanced compound thin films and coatings, made with parametrically controlled laser ablation pulses, could be significantly advanced through the application of several *in-situ* characterization and control methodologies. It is anticipated that this approach will provide significant process control, through real-time feedback, in manufacturing DoD related products such as multilayer thin films and coatings.

Reliable development of structured layers can be achieved through the systematic use of stabilized manufacturing processes. Experimental facilities employing such techniques, in conjunction with other more conventional particle monitoring and control methods, will provide new and advanced capability, as well as greater insight, into complex thin-film fabrication. Such

insight has been, and continues to be, demanded by sophisticated industrial and government end users. The present project is aimed at establishing a multi-port pulsed laser vacuum deposition chamber with an in-situ multi-wavelength ellipsometer to be used as an optical diagnostic and feedback control device. This system is attached to a versatile high average power ultrafast pulsed laser for the experimental development and fabrication of modulated thin-film materials and multilayers. It is intended to be a collaborative and interdisciplinary research facility set up at the Center for Ultrafast Optical Science at the University of Michigan.

2.0 Equipment Purchased

The following major equipment items have been purchased under this funded project :

Varian Turbo-Molecular Pump (with diaphragm backing pump) $12,618
J.A.Woollam in-situ Spectroscopic Ellipsometer $46,150
Thermionics Northwest- Vacuum Substrate and Ablation Target Manipulators $61,787
Thermionics Vacuum chamber- design, construction, and delivery $15,689
Newport Translation Stage $4,158
Computer- multifunction analog board $1,435
Fabrication and assembly costs $4,349

The total budget for this program was $146,186 of which the Air Force provided $101.186 and the University of Michigan provided $45,000. The total funds spent on this project has been $146,186.

Personnel who worked on this project (but whose salaries were not funded by it) were Peter P. Pronko (principal investigator) and Paul A. Van Rompay (graduate student). Various undergraduates participated in the equipment development and testing as part of summer research projects and undergraduate research experience programs at the University of Michigan.

3.0 System Status

Status of equipment, as of Oct. 1997, with associated subsystem components and items for final assembly, is depicted in Figures 1 and 2 below. Figure 1 shows a picture of the deposition facility in its anticipated final configuration. This photograph is provided by Thermionics, Inc., from whom the major equipment items were purchased, and is a close representation to what our system will look like when completed. The long arm extending to the left in the picture is the vacuum loadlock arm which is not being purchased as part of the present project. It is intended that this item be obtained under a future project. The mechanism on top is the substrate mount and manipulator. The arm extending to the right, which is mounted on the large flange is the multi-target ablation stage. This part of the system is shown retracted on the flange dolly-track assembly. The multiple ports on the vacuum chamber are available for laser access, diagnostic probes(such as our spectroscopic ellipsometer and other probes), as well as for physical and mechanical access to the interior of the chamber. This entire system is floor mounted on a steel frame sub-system that can rest securely to the floor or be lowered onto wheels for transport into other experimental areas. Figure 2 shows a composite view of components that were acquired under the DURIP grant being reported upon and which will contribute to making up our final facility. In Fig. 2A is seen our substrate mount and manipulator which is currently set up on a small horizontal vacuum chamber that is providing early experimental capability on thin film fabrication. This chamber is evacuated with the same turbo pump that will be used on the final facility. Presently experiments are under way on making BN films. A single ablation target is used in this chamber which is mounted on a small internal DC motor with 1e-7 torr vacuum capability. To the right in picture A and beyond the deposition chamber is seen the UHV vacuum chamber which was obtained from Kirtland AFB (Vern Schlie) and in which is presently mounted a sector field electrostatic analyzer. This unit is attached directly to the

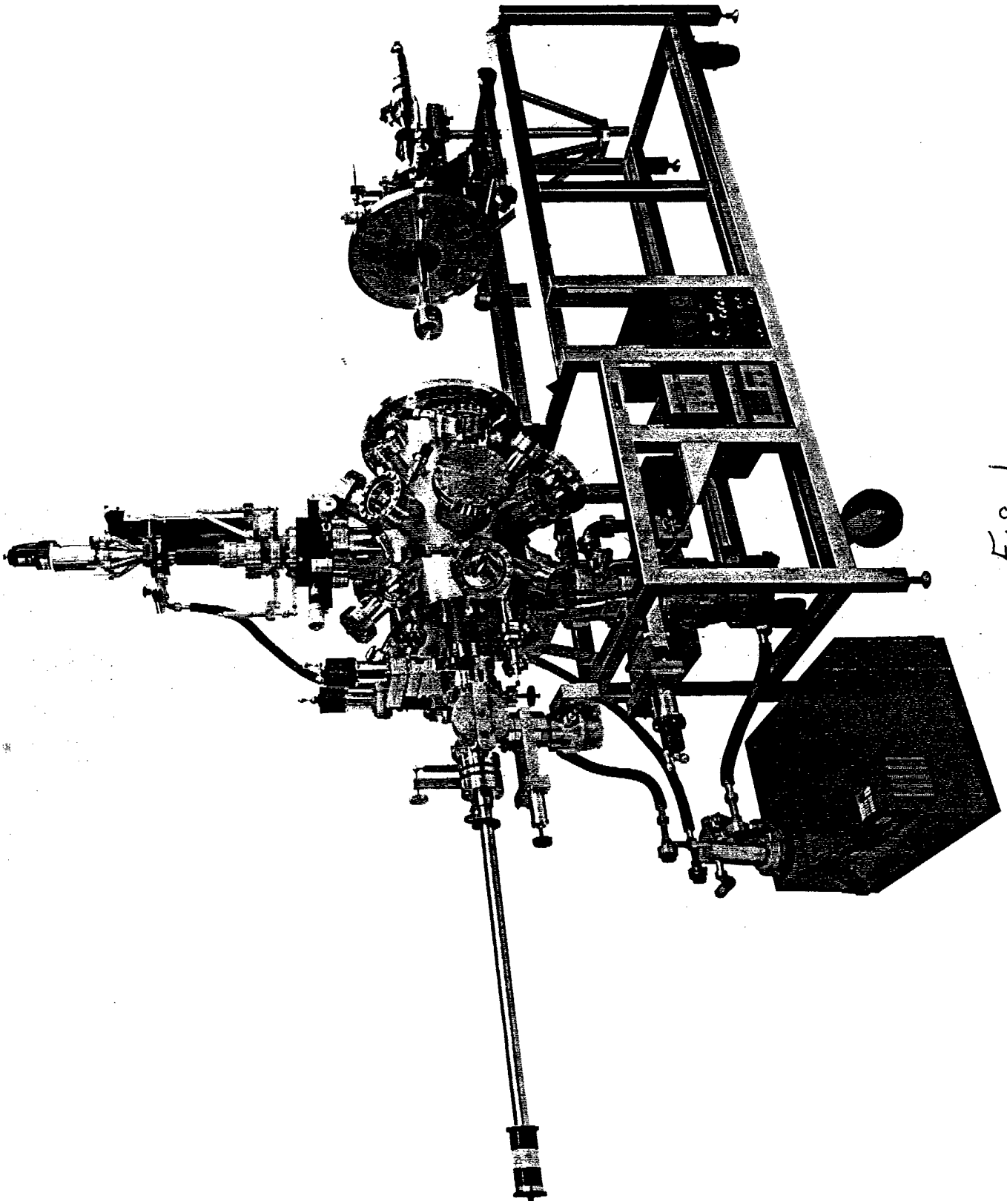
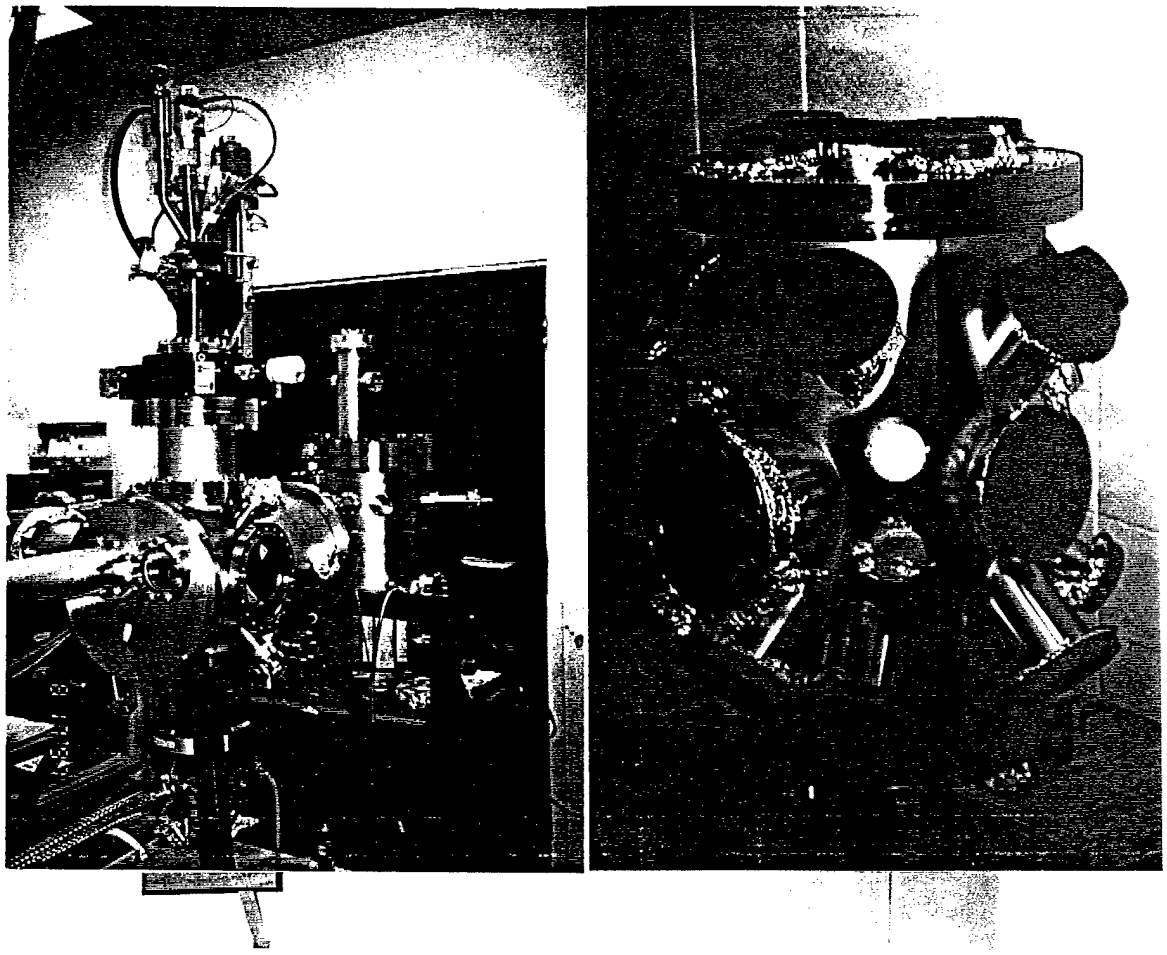
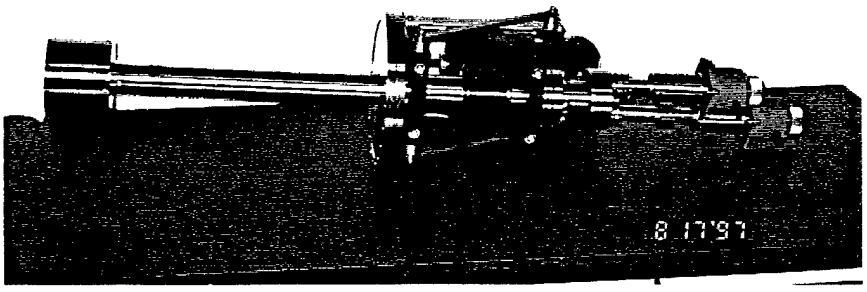


Fig. 1



A

B



C

Fig. 2

ablation chamber for experiments on the characteristics of ion species and energies within the ablation plume. An example of data from this unit is presented in Section 4 below. In the picture of Fig. 2B is seen our large, and as yet, unassembled vacuum chamber which will take the place of the small horizontal chamber in the picture of Fig. 2A. It will rest on the frame as depicted in Fig. 1. In the picture of Fig. 2C is shown our multi-target ablation stage which will mount on the large 22 inch end flange (as seen on the flange dolly of Fig. 1). Since ultrashort laser pulses are intended to be used in this system, it will be necessary to include magnesium fluoride windows for transmitting the beam into the chamber as well as all reflective optics, inside the chamber, for focusing the beam. Thin transparent protective shielding will be required inside the chamber to protect optical components from spurious ablation plume products. Designs with such considerations are currently under way. Final assembly of the components in Fig. 2 is currently underway using operating funds supplied by the Center for Ultrafast Optical Science at the University of Michigan. Functional status is expected at the end of the 1997 calendar year.

4.0 Research Performed to Date

Work in the area of ultrafast laser ablation plume generation and thin film deposition has been progressing while the present advanced deposition facility was being acquired and assembled. Subsystem components from the subject DURIP project were used in several instances. In this section we present research titles and abstracts of ongoing work, by the principal investigator and members of his group, that are relevant to the subject of this report.

I. "Carbon Ion Charge States and Energy Distributions for DLC Ablation Plumes
from 100 fs 780 nm Laser Pulses"
Surface Science and Coatings Technology (accepted for publication)
Presented at the European-Materials Research Society Conference
Strasbourg, FR., June 1997

A time-of-flight, sector field, electrostatic analyzer has been used to obtain detailed information about the ionic charge states of carbon for laser ablation plumes typical of those used for depositing diamond-like carbon (DLC) films. Time resolved spectra from the E/q analyzer are used to construct energy distributions of individual charge states of the various carbon ions. The measurement range of the detector is from 0.05 to 20 keV per unit charge, allowing for observation of up to 80 keV at charge state four. (See Fig. 3).

II. "Pulse-Contrast Effects on Energy Distributions of C^{1+} to C^{4+} Ions
for High-Intensity 100 fs Laser-Ablation Plasmas"
Applied Surface Science(accepted for publication)
Presented at the 4th International Conference on Laser Ablation
(COLA ' 97), Asilomar, CA, July 1997

It is observed, for 100 fs laser pulses at 780 nm and in the 10^{14} to 10^{16} W/cm^2 intensity range, that the characteristics of the ion energy distributions are highly dependent on the peak-to-background contrast ratio of the laser pulse as well as the presence of any additional pre-pulse. Ion energies are observed and examined in the kinetic energy range from 100 eV to 20 keV. A bi-modal energy distribution is obtained for high contrast pulses and interpreted in terms of a plasma hydrodynamic model for the lower ion energies (few hundred eV) and an ambipolar field-accelerated ion contribution for the higher energies (several keV), (See Fig. 4).

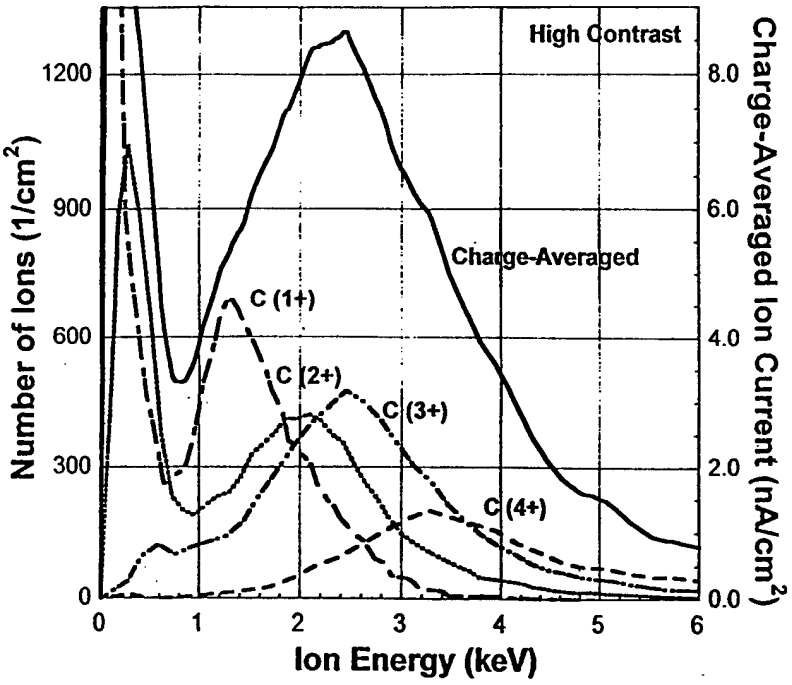


Figure 3.
Ion energy distributions separated by charge state and charge averaged for carbon ablation with 100 fs, 10^{15} W/cm^2 laser pulses. The low energy distribution can be explained by a hydrodynamic expansion process, and the high-energy distribution by a plasma ambipolar ion-acceleration process.

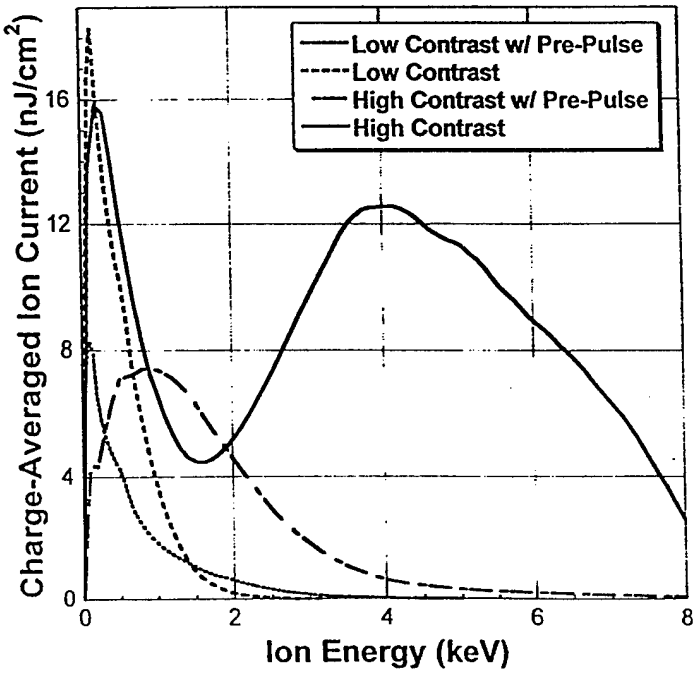


Figure 4.
Measured charge-averaged ion energy distributions for a laser intensity of 2 x 10^{15} W/cm^2 at four laser conditions with high/low contrast ($10^6/10^5$) and with or without a pre-pulse (ultrashort pulse with 1/10 the laser energy at 9 ns before main pulse).

III. "Femtosecond Laser Deposition of Diamond-Like Carbon Films"
Materials Research Society Symposium Proceedings, 397 297 (1996) and
Applied Physics Letters 67 3120 (1995)

Unhydrogenated diamond-like carbon (DLC) films have been deposited with 100 fs laser pulses at intensities in the 3e14 to 6.5e15 W/cm^2 range. Film surface topography, optical properties, and bonding structure were examined, respectively, with atomic force microscopy (AFM), spectroscopic ellipsometry (SE) and Raman spectroscopy. The most probable kinetic energy of carbon ions was estimated to be in the 300 eV to 2 keV range, increasing with laser intensity. In addition, a unique "suprathermal" component with kinetic energy ranging from 4 to 40 keV was observed in the TOF spectrum. This high energy peak is believed to originate from fast ions in a solid density plasma created during the absorption of each femtosecond laser pulse. High quality diamond-like carbon was produced at the optimum laser intensity of 3e14 W/cm^2.

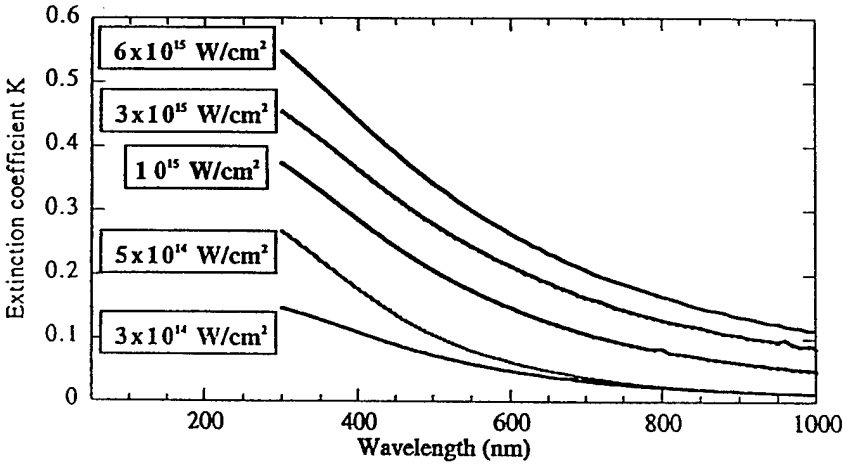


Figure 5.

Extinction coefficient k of DLC as a function of wavelength and laser intensity. It is observed through these results that the better DLC films (i.e. least absorption) are obtained with lower laser intensities where plasma plume ion energies are optimized.

IV. "Laser Induced Avalanche Ionization and Electron-Lattice Heating of Silicon with Intense Near IR Femtosecond Pulses"
(Materials Research Society Symposium Proceedings 397 45 (1996) and
Ultrafast Phenomena Conference, San Diego, May 1996

A two temperature finite difference model has been developed and is used to describe the response of materials under ultrafast femtosecond laser pulses in the energy regime where melting and vaporization can occur. In applying this model to silicon it is observed that, for 800 nm light, laser pulse intensities that are just sufficient to achieve threshold for vaporization are also at the level of optical electric field strength where electron avalanche breakdown at the surface of the material can occur. For sub-picosecond pulses the physical response of the

material is associated with a strongly temperature dependent coupling coefficient connecting electron and phonon thermal distributions. The results of these analyses demonstrate that a very thin near solid density plasma, caused by avalanche ionization, is responsible for the surface heating and subsequent thermodynamic response of the material. This interpretation is consistent throughout the pulse duration range from 80 femtoseconds to 0.2 nanoseconds. The proposed mechanism for absorption, at the near infra-red wavelength being used here, is very different from the types of mechanisms usually considered for nanosecond laser heating of semiconductors. Surface damage threshold is determined by atomic force microscopy and the threshold for plasma optical emission by photomultiplier detection .

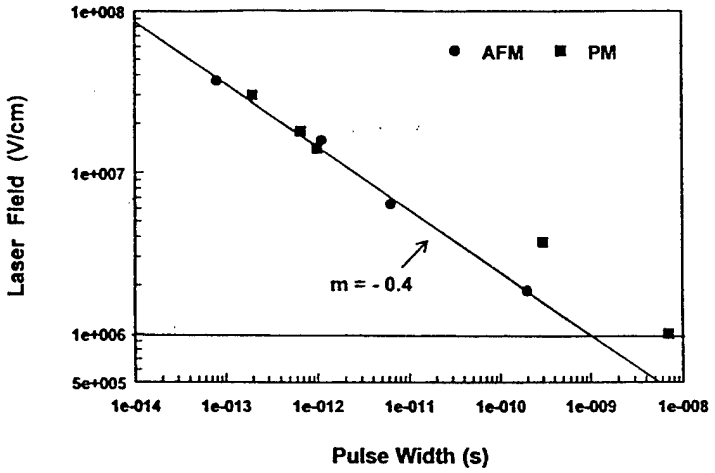


Figure 6. Measured AC (rms) breakdown electric field strength in silicon as a function of laser pulse duration. AFM=atomic force microscope data, PM=photomultiplier data and m = slope of fitted line.

5.0 Evolution of the System

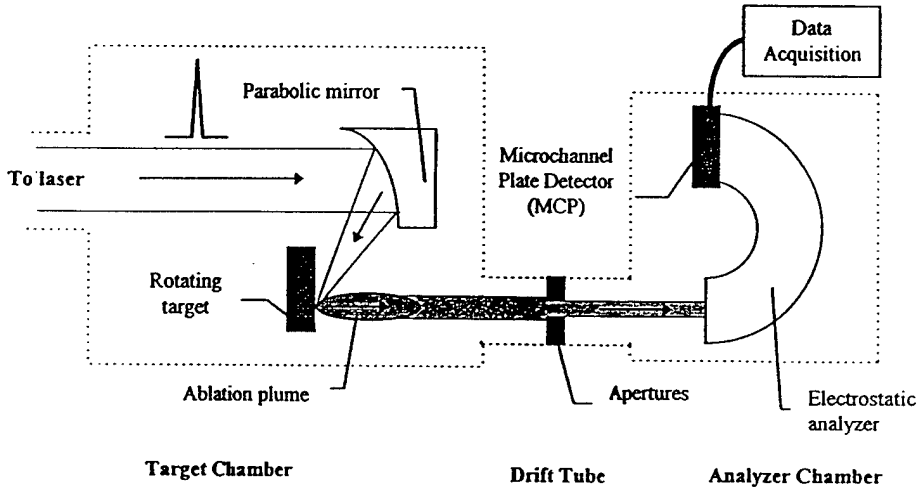
It is expected that, with supplementary support, the deposition system, which originated with the DURIP '95 project, will ultimately develop into a full operational state as shown in the photograph of Figure 1. In addition, it is expected that a complementary set of diagnostic equipment will be added to the facility in order to guarantee optimum growth parameters for the fabricated films. These additions will be provided for through a combination of CUOS center funds and funds being sought through additional proposal submissions. In particular, a follow-on DURIP '98 proposal has been submitted to AFOSR in regard to this ongoing endeavor. That particular proposal is requesting funds for an *in-situ* RHEED system and a UHV vacuum sample load-lock assembly.

6.0 Planned Experiments

Nitride Compounds:

Our plans for experiments in the immediate future involve the investigation of wide band gap materials and hard coatings for high temperature applications. An attractive class of materials in this category can be found in the systems that include Boron, Silicon, Aluminum, Carbon, and Nitrogen. Binary and ternary compounds from this system form an interesting and potentially useful group of polymorphic materials that include BN, SiC, AlN, and CN for the binaries, and BCN, SiAlN, BSiN and BAlN for the ternaries. Initially work will be restricted to the nitride based systems since a separate chamber will be required to process carbide based

materials in order to eliminate cross contamination between films. These systems provide a rich and varied base from which to launch an aggressive materials science oriented program. As an example of these type studies, we have obtained ion charge state and energy distributions from laser plasma plume spectra of sintered BN starting material using our spherical sector electrostatic analyzer. An example of these data are presented in Fig. 7 for a laser intensity of 1e14 W/cm^2 at 100 fs pulse duration.



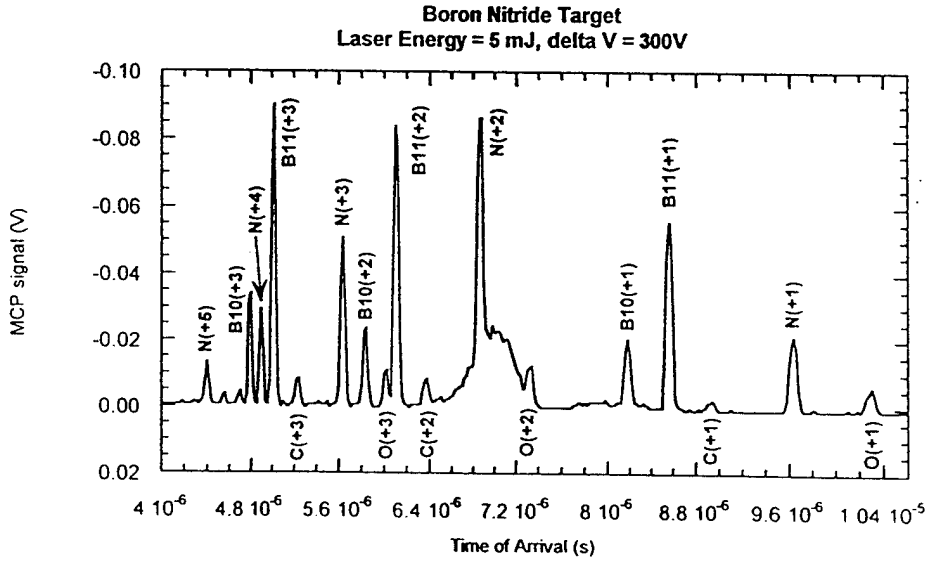


Figure 7 - Electrostatic analyzer and associated time resolved E/q analyzer spectra for BN ablation for a laser intensity of 1e14 W/cm^2 at 100 fs pulse duration.

It is determined from a collection of spectra as a function of analyzer energy, like that of Fig. 7, that not only are high charge states generated but high energies and near totally dissociated nitrogen is obtained in the ablation plume. The spectrum in Fig. 7 shows no N_2 ions but a high concentration of N^{n+} (n=1 to 3) in the plasma plume. Experiments are now planned to examine how these spectra change as the partial pressure of nitrogen background gas is increased in the deposition chamber. The analyzer has also been fitted with a straight through port to analyze the neutral component by time of flight techniques. It is interesting to note that several recent research reports at the E-MRS and COLA ' 97 conferences contained papers

demonstrating early valuable results from laser ablation deposition of nitride based thin films and coatings, however extensive research is still needed in this subject area.

Nano-Composite Films:

Another area of anticipated use for the system is in deposition of nano-scale thin film composites. It is predicted by theory that such materials could have enhanced mechanical and hardness properties. In such experiments on composite refractory metal films using sputter deposition, it has been found that less than theoretical density is usually obtained. Also, columnar growth within the films is often observed. These problems conspire to yield mechanical properties of free standing films fabricated by this method that fall short of the theoretical predictions for enhanced mechanical properties for these materials. Since the final composite material is made up of many hundreds of nano-layers, the columnar growth is averaged out by being terminated at the thin layer boundaries. However, the reduced density remain as a compromising problem. This latter difficulty can be addressed by use of energetic ion beam bombardment during deposition in order to simultaneously densify the films while they are growing. Laser ablation deposition with a multi-ablation target assembly as described above and shown in Fig. 2 C is an excellent candidate for exploring solutions to these low density problems. As discussed above and shown in Fig's 3, 4, and 7, the ultrafast laser ablation plumes contain a significant fraction of high energy ions that are available for simultaneous ion bombardment and densification during deposition. In fact, this is where the ultrafast lasers can make a very significant contribution, since the ablation plumes have a measured high energy component in the KeV range (a plasma accelerated component). This high energy distribution (which is controllable) is superimposed on top of a conventional hydrodynamic plume that is in the energy range of a few hundred eV or less. The low energy component would provide the material for the film deposition, while the high energy component densifies it. The multiple ablation targets, being activated and cycled into the laser beam by computer control, provide a uniquely valuable approach to the process technology. A very large number of thin (100 angstrom) alternating type films could be uniformly deposited over our two inch diameter substrate, during the fabrication of self supporting inter-metallic composites. Examples of systems that could be studied are Titanium Aluminides alternating with Niobium compounds for future development of high temperature refractory materials for potential use in aerospace vehicles and aircraft.

APPENDIX I.

Progress Report
AFOSR - DURIP
10/11/96

Award Reference Number
F49620-95-1-0474

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PROGRESS REPORT 10/11/96

"Advanced Pulsed Laser Deposition System with in-situ Ellipsometric Diagnostics"

Funds were provided in this program for part of what is intended to become a larger system representing an optics based research facility for ultrafast pulsed laser deposition and characterization of modulated films, coatings, and surface structures.

The objective of the AFOSR part of the project is to establish a multi-port, pulsed laser ablation, vacuum deposition chamber with an in-situ multi-wavelength ellipsometer (to be used as an optical diagnostic and feedback control device). This system is to be attached to a versatile high average power ultrafast pulsed laser for the experimental development and fabrication of modulated thin film and multi-layered materials.

Progress to date consists of procuring the following major equipment items:

Varian Turbo-Molecular Pump (with diaphragm backing pump) $17, 376.11
J.A.Woollam in-situ Spectroscopic Ellipsometer $46, 150. 00
Thermionics Northwest- Vacuum Substrate and Ablation Target Manipulators $60, 652.75

In addition to these, a total amount of $10,905.43 has been spent on fabrication of components and support items to be used in conjunction with the above described major equipment items. Used in concert, these fabricated items, and the associated pieces of major equipment, constitute the sub-system intended for construction.

Remaining to be designed and purchased is a ultra high vacuum deposition chamber to which the ellipsometer, ablation manipulators, and turbo-molecular pump will be mounted. We are in the final stages of accomplishing this objective.

The total budget for this program was $146,186.00 of which the Air Force provided $101.186.00 and the University of Michigan provided $45,000.00. The total funds spent and encumbered is $135,084.29 The funds remaining to be used for the vacuum deposition chamber are $11,101.71.

Personnel on the project include Peter P. Pronko (principal investigator) and Paul Van Rompay (graduate student)